

RELATION OF COAL LIQUEFACTION CATALYST PROPERTIES TO PERFORMANCE

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INTRODUCTION

In March 1975, Amoco Oil Research, under contract with EPRI, began a three-year project on liquefaction catalysis (1,2). The specific purpose was to develop one or more superior catalysts for hydroliquefaction processes in advanced stages of development, such as the H-Coal process. The primary interest was in the conversion of coal to a clean-burning boiler fuel, low in sulfur and ash.

The hydroliquefaction of coal is a complex process which involves close interaction between the solubilized coal, hydrogen donor solvent, and catalyst. An improved catalyst for coal liquefaction must satisfy several requirements, but two key aspects are high initial activity for liquefaction-desulfurization and good aging characteristics.

Initial catalyst performance was determined in a batch test unit. A large number of catalysts, both commercially available and experimental, have been screened for initial performance. Catalysts selected on the basis of their physical and chemical properties as well as initial performance in the screening test were then subjected to continuous flow operation for approximately one week to determine their early deactivation behavior. Good initial performance of a catalyst may rapidly decline due to factors such as coking, sintering and metals deposition. Therefore a crucial aspect in developing a coal liquefaction catalyst is continuous operation for extended periods.

EXPERIMENTAL

Batch Screening Unit

The screening of catalysts for initial performance was carried out in a one-liter stirred autoclave. A mixture of 10 grams of catalyst (60-100 mesh granules, predried), 150 g coal and about 300 g liquefaction solvent was charged to the autoclave at ambient conditions. The coal was Illinois No. 6 from Burning Star Mine, ground to pass a 40 mesh screen. The solvent consisted primarily of mono-, di-, and trimethylnaphthalenes derived from petroleum refining and was essentially free of sulfur, nitrogen and oxygen. Pressure, hydrogen flow rate and mixing speed were set and reactor temperature was raised to 750°F in about 60 minutes. After

reaction at that temperature for 40 to 60 minutes, the reactor was cooled rapidly for removal of the reactor contents at ambient conditions. The test conditions are listed below.

Catalyst Screening Conditions

Catalyst	10g, 60-100 mesh
Coal, Illinois No. 6	150g
Solvent	300g
Pressure	2000 psig
Hydrogen flow rate	3 ft ³ /hr
Mixing speed	1800 rpm
Temperature (maximum)	750°F
Reaction time at 750°F	40-60 minutes

Product Workup and Analysis--Batch Unit

Evaluation of catalyst performance was based on the following procedure for separating liquid product from solid residue. The reactor contents were vacuum filtered and the filtrate segregated. Residual material was recovered from the reactor with benzene and washed through the filter cake. After additional washing with benzene, the filter cake and paper were Soxhlet extracted for 16 hours with benzene. The benzene solutions were combined and distilled to recover an extract that was added to the original filtrate. The final liquid which contains coal product, liquefaction solvent and a small amount of residual benzene was subjected to elemental analysis to determine product quality. The analysis was corrected for water and benzene present. The solid residue was dried at 160°C in a vacuum oven. A moisture and ash free conversion was defined on the basis of solid residue with the assumption that any change in the weight of the catalyst, which was not separated from the coal residue, would be of minor importance. Conversion, thus defined, has been referred to as benzene soluble conversion although, strictly speaking, the filtered product initially segregated in the product workup contained some converted material that is insoluble in benzene.

Catalyst Performance Indices--Batch Unit

Liquefaction conversion and the sulfur content of the coal liquid were used as the primary indicators of catalyst performance. The results obtained in the absence of catalyst provided the reaction baseline while Filtrol cobalt-molybdenum on alumina was selected as the reference for comparing initial catalyst performance.

Under otherwise constant conditions, conversion of coal to liquid product depends on reaction time and whether or not a hydrogenation catalyst is present. Simple reaction kinetics do not define the increase in conversion with increasing reaction time. Hence, some means other than the reaction rate constant is needed to assess catalyst activity. If the conversion obtained without added catalyst can be viewed as the result of noncatalyzed or thermal reaction, then at any given reaction time the increased conversion obtained with catalyst present is indicative of catalyst performance. The ratio of this increase to that obtained with the reference catalyst, Filtrol HPC-5, is defined as the conversion index.

There is also a corresponding decrease in product sulfur content as reaction time is increased. As with conversion, a desulfurization index can be defined as the decrease in product sulfur from the noncatalyzed baseline relative to that obtained with the reference catalyst at the same reaction time.

Continuous Testing Unit

The continuous pilot plant consists of three main sections as shown in the flow diagram (Figure 1). The first section called the feed module contains all equipment for feeding coal slurry and high pressure hydrogen. The center section which is the reactor module contains a 1-liter stirred autoclave and liquid product recovery system. The third module contains the gas let-down, metering and sampling facilities. The design conditions include a maximum working pressure and temperature of 4000 psig and 900°F. Once-through hydrogen is used in the catalyst activity test, but gas recycle has been provided. The once-through operation is preferred for aging tests since hydrogen pressure is maintained constant, independent of the light ends production.

The combined stream of coal slurry and hydrogen gas is continuously introduced into the bottom of the liquefaction reactor and reaction products withdrawn through a vertical overflow tube. A schematic of the reactor is given in Figure 2. Reactor holdup can be varied by changing the overflow tube height. A 60 cc catalyst charge is retained in a stationary annular basket. A specially designed blade impeller plus high agitation rate assures good mixing and contacting of the coal slurry with the catalyst.

Test Conditions--Continuous Unit

The nominal operating conditions used for catalyst testing in the continuous pilot plant are as follows:

Catalyst Test Conditions

Pressure	137 atm (2000 psig)
Temperature	427°C (800°F)
Hydrogen feed rate	170 liters/hr (6 scfh)
Slurry feed rate	400 gm/hr
Slurry concentration	20 wt%, -400 mesh coal (Ill. #6)
LHSV	1.33 gm coal/hr - cc cat
Residence time	48 minutes
Catalyst charge	60 cc
Mixing speed	1500 rpm

Product Workup--Continuous Unit

Product workup required considerable attention in this catalyst development program. To measure catalyst performance, one needs information on coal conversion and product quality. However, the information must satisfy certain requirements specific to the development program. This includes control of the aging test, a rapid measurement based on a small sample, and evaluation of the product quality, using a larger sample.

Coal liquids are normally characterized by solubility in a given solvent. Insolubles in coal product may be determined by different procedures which vary in extraction solvent; therefore, the solvent used defines conversion.

The product workup methods selected include two micro and one macro residue method using benzene and tetrahydrofuran (THF). Conversion based on the micro-benzene method (pressurized filtration using millipore cartridge filter) provides a quick index of product quality. Benzene soluble materials, such as asphaltenes and oils, represent the upgraded fraction of boiler fuel. Conversion based on the micro-THF method measures boiler fuel yield. Detailed evaluation of the liquid coal product requires a larger sample for boiling range determination and elemental analysis. The macro-THF residue method (Soxhlet extraction) is used for this purpose.

DISCUSSION

BATCH SCREENING RESULTS

Cobalt-Molybdenum Composition

The effect of varying the cobalt-molybdenum composition was examined to determine if the optimum catalyst composition for coal liquefaction might be different than that typically used in commercial desulfurization catalysts and to gain an indication of the impact of differences in catalyst composition on performance in the screening test. The study was made with two alumina supports having different surface properties--Cyanamid PA (ca. 300 m²/g, 60 Å) and Kaiser KSA Light (ca. 180 m²/g, 160 Å).

With both aluminas, conversion index increased rapidly up to about 10 wt% MoO₃ and then very slowly at higher molybdena contents (Figure 3). Both catalyst systems responded similarly to cobalt with the optimum lying between 2 and 4 wt% CoO. The Kaiser alumina, however, provided a more active catalyst than Cyanamid PA.

For desulfurization, the two supports were indistinguishable (Figure 4). Like conversion, desulfurization index increased rapidly up to about 10 wt% MoO₃ but then leveled off as molybdena content was increased further. The optimum cobalt content for desulfurization was also between 2 and 4 wt% CoO. However, desulfurization was much more sensitive than conversion when the cobalt content was reduced to zero.

Since catalysts made with two supports having different surface properties showed a similar relationship of performance to composition, it appears reasonable that a single composition of, say, 3 wt% CoO and 15% MoO₃ would be appropriate for studying the effects of the support on initial catalyst performance. Furthermore, small deviations from this composition should have only a minor effect on catalyst performance.

Surface Property Effects

The study on surface properties of cobalt-molybdenum catalysts focused primarily on the surface area and average pore diameter. These surface properties are considered important because the number of catalytic sites available depends on surface area and the accessibility of these sites is limited by the pore structure. Average pore diameter is an indicator of pore structure although the distribution of pore sizes may well be more important.

Consider, for example, the relationship of initial performance to the structural properties of the alumina supported catalysts. With respect to surface area, conversion index (CI) is relatively constant over a wide range while desulfurization index (SI) increases with increasing surface area (Figure 5). A corresponding disparity of performance is shown with respect to average pore diameter (Figure 6). The preferred average pore diameter for desulfurization appears to be smaller than for conversion.

These observations provide a basis for selecting catalysts for continuous testing. There is admittedly some scatter in the data which might be resolved by a closer look at such factors as pore size distribution. However, appropriate choices for determining the relation of activity maintenance to surface properties should include aluminas with average pore diameters in the range of 100 to 200 Å.

DISCUSSION-- CONTINUOUS TESTING RESULTS

The short-term aging behavior will now be discussed for a variety of catalysts tested in the continuous pilot plant. The main catalyst parameters we have focused on are surface properties, impregnating procedures, and type of catalytic metals.

Surface Properties and Impregnation Procedures

The effect of surface properties and impregnating methods was investigated by impregnating a series of alumina supports with cobalt and molybdenum. A phosphoric acid impregnating aid was used in some cases to adjust the acidity of the impregnating solution. Again, to facilitate data interpretation, surface area and average pore diameter were the two parameters used to characterize the surface properties, although the distribution of pore sizes should also be considered. The various CoMo on alumina catalysts tested are listed in Table I.

Table I. CoMo on Alumina Catalysts

<u>Catalyst ID*</u>	<u>Major Pores Å</u>	<u>APD Å</u>	<u>SA m²/g</u>	<u>PV cc/g</u>	<u>ABD g/cc</u>
HDS-1442 (ref)	30-110	58	323	.56	.57
KSA-LP	50-250	105	195	.70	.59
Grace-100UP	60-200	118	140	.54	.69
Grace-200UP	110-300	187	78	.44	.75
Grace-100U	60-200	122	167	.59	.68
Grace-200U	110-300	202	92	.52	.73

*U: unimodal; P: phosphorus addition

Referring to Figure 7, we compare liquefaction conversion for the various catalysts to the reference catalyst, HDS-1442A. First of all, the larger pore catalyst, Grace-200UP, results in higher conversion than the smaller pore version, Grace-100UP. The catalyst based on Kaiser KSA-LP alumina exhibits a rapid decline in activity even though its APD is around 100 Å. Closer inspection of the pore size distribution reveals that the KSA-LP alumina has a broad distribution of pore sizes.

The elimination of the phosphoric acid impregnating aid causes an upward shift in conversion for the catalyst prepared with Grace-100U alumina. However, no improvement was observed on the large pore Grace-200U alumina by eliminating the phosphoric acid. Therefore the best liquefaction performance is achieved with an alumina having an APD and surface area of 100 Å and 200 m²/gm, respectively. Furthermore, a phosphoric acid impregnating aid is detrimental to the liquefaction performance.

Desulfurization performance of the catalysts was evaluated by monitoring the sulfur content of the resid fraction (975°F+) of the coal liquid product. Referring to Figure 8, the lowest sulfur level was achieved with the catalyst prepared on Grace-100U alumina. We again conclude that the Grace-100U alumina gives the best overall performance.

Alternate Catalytic Metals

A series of catalyst tests to explore the effects of varying hydrogenation and cracking activity was also performed. Alternate hydrogenation metals tested include Ni-W, Ni-Mo, Ni-Mo-Re, all supported on the small pore Grace 100 alumina. Cracking activity was increased by impregnating the alumina with silica prior to impregnation with the catalytic metals. The specific version tested was a Ni-Mo on a silica promoted alumina. Inspections for the catalysts employing alternate catalytic metals are listed in Table II.

Table II. Catalyst Inspections--Alternate Hydrogenation Metals

<u>Catalyst</u>	<u>Composition</u>	<u>APD Å</u>	<u>SA m²/g</u>	<u>PV cc/g</u>	<u>ABD g/cc</u>
HDS-1442A	3.1 CoO-13.2 MoO ₃	58	323	.64	.57
Grace-100U	2.9 CoO-16.8 MoO ₃	122	167	.59	.68
NiW-100U	3 NiO-25 WO ₃	118	140	.52	.75
NiMo-100U	2.0 NiO-16.2 MoO ₃	119	163	.62	.67
NiMoRe-100U	3 NiO-16 MoO ₃ -2.3 Re	113	158	.58	.69
NiMo-100U/Si	3 NiO-16 MoO ₃	---	---	---	.66

Benzene soluble conversion is plotted against time on stream in Figure 9 for all of the catalysts in Table II. Compared to the cobalt-molybdenum catalyst (Grace-100U), both NiMo and NiMoRe gave lower benzene soluble conversion and faster decline rates. Addition of rhenium to NiMo had little effect. The more acidic support, silica promoted alumina,

did not improve performance of nickel-molybdenum. The increase in benzene soluble conversion of NiMo catalysts over the reference HDS-1442A catalyst can probably be explained by more favorable surface properties and higher density. Nickel-tungsten gave the lowest benzene soluble conversion which confirmed previous batch screening results.

CONCLUSIONS

Effective tests have been developed to evaluate coal liquefaction catalysts and relate their performance to catalytic properties. Initial performance in the batch unit was related to metals loading of cobalt and molybdenum and surface properties, specifically average pore diameter and surface area. Aging behavior of liquefaction catalysts was established for several catalysts in a continuous pilot plant unit. Surface properties had the most pronounced effect on aging performance; type of catalytic metals appeared to be a secondary effect.

REFERENCES

1. Brooks, J. A., Bertolacini, R. J., Gutberlet, L. C., Kim, D. K., "Catalyst Development for Coal Liquefaction," Electric Power Research Institute First Annual Report AF-190, February, 1976.
2. Bertolacini, R. J., Gutberlet, L. C., Kim, D. K., Robinson, K. K., "Catalyst Development for Coal Liquefaction," Electric Power Research Institute Second Annual Report, October, 1977.

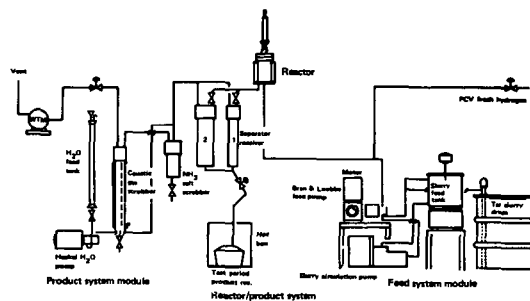


Fig 1 Unit flow diagram

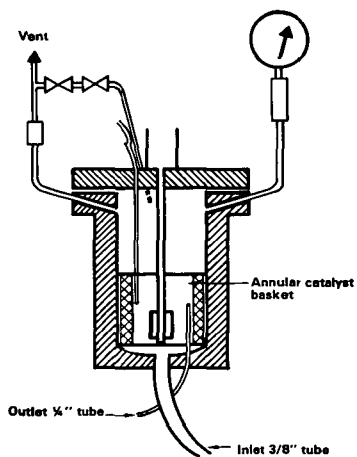


Fig 2 Liquefaction reactor

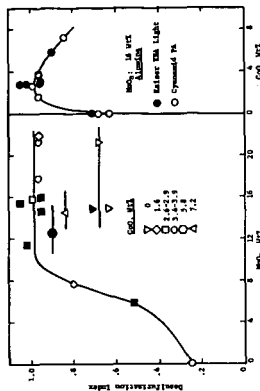


Figure 4. Effect of Catalyst Composition on Desulfurization Index

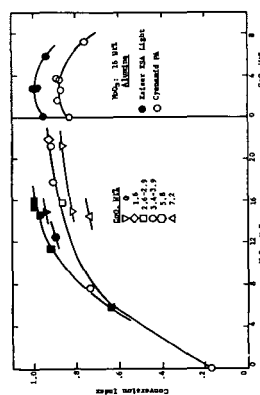


Figure 3. Effect of Catalyst Composition on Conversion Index

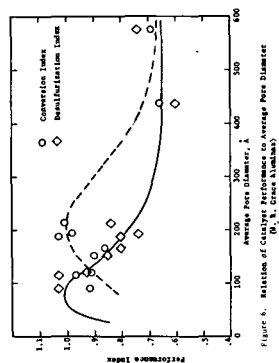


Figure 6. Relation of Catalyst Performance to Average Pore Diameter (N. H. Green Alundmax)

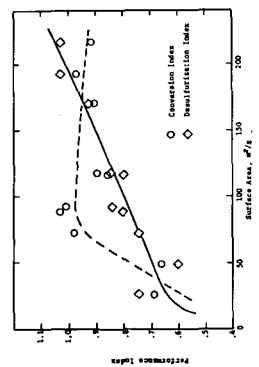


Figure 5. Relation of Catalyst Performance to Surface Area (N. H. Green Alundmax)

